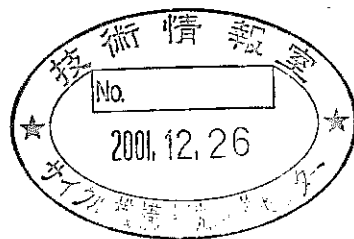


# Determination of Gibbs Energy of Formation of $\text{Na}_3\text{FeO}_3$ by High Temperature Mass Spectrometer



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## Determination of Gibbs Energy of Formation of $\text{Na}_3\text{FeO}_3$ by High Temperature Mass Spectrometer

Jintao HUANG\*, Tomohiro Furukawa\* and Kazumi Aoto\*

### Abstract

Sodium-iron complex oxides are likely to form if sodium-leak incident occurs in Fast Breeder Reactors. Thermodynamic data of these compounds are very essential to analyze corrosion mechanisms in various environmental conditions. Though Na-Fe-O system has been investigated for several decades, unfortunately experimental data of  $\text{Na}_3\text{FeO}_3$  and  $\text{Na}_5\text{FeO}_4$  are still very limited to get a complete understanding. So, a high temperature mass spectrometer was set up to obtain reliable thermodynamic data of these sodium-iron complex oxides.

To obtain reliable data, careful attention was paid to the material of the sample container, i.e., the Knudsen cell. Platinum was selected by experiments as cell material because it showed good chemical compatibility with sodium compounds until 1473 K.

To guarantee reliability of the measurement system, preliminary measurement over pure sodium was done first as a reference test. Saturated vapor pressure of pure sodium was measured from 390 to 470 K. Satisfied precision of vapor pressure measurement is confirmed.

Then, a decomposition reaction of  $\text{Na}_4\text{FeO}_3(\text{s}) \rightarrow \text{Na}_3\text{FeO}_3(\text{s}) + \text{Na}(\text{gas})$  was studied by high temperature mass spectrometry. Temperature dependence of sodium vapor pressure was determined as  $P_{\text{Na}}/\text{Pa} = 3.8589 \times 10^{10} \exp(-17749/T)$  in the temperature range of 590-717 K. Thermodynamic functions related to the reaction were determined as follows,

$$\Delta_r H^\circ(653\text{K}) = 148.5 \text{ kJ/mol and } \Delta_r G^\circ(T) = 148522 - 108.29 \times T.$$

Based on thermodynamic data of  $\text{Na}_4\text{FeO}_3$  given in literature, the Gibbs energy of formation of  $\text{Na}_3\text{FeO}_3$  was evaluated as,

$$\Delta_r G^\circ(\text{Na}_3\text{FeO}_3) = -1168629 + 338.34 \times T.$$

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## 高温質量分析計による $\text{Na}_3\text{FeO}_3$ の生成ギブズエネルギーの評価

黄錦涛\*、古川智弘\*、青砥紀身\*

### 要 旨

ナトリウム冷却高速増殖炉でナトリウム漏えい事故が生じた場合、漏えいナトリウムによって構造材料が腐食され、反応生成物としてナトリウム・鉄複合酸化物 (NaFe 複合酸化物) が形成される。この NaFe 複合酸化物の熱力学データは、いろいろな漏えい環境条件における腐食メカニズムを評価していく上で必要とされる。しかしながら、Na-Fe-O 系に関する研究は、数十年間実施されてきているものの、 $\text{Na}_3\text{FeO}_3$  や  $\text{Na}_5\text{FeO}_4$  の熱力学データについては十分な実験結果が得られていない。そこで、著者らは、NaFe 複合酸化物の信頼性の高い熱力学データを取得するために、クヌーセン・セルと高温質量分析計を組み合わせた蒸気圧測定装置を開発した。

信頼性の高いデータを取得するために、試料容器となるクヌーセン・セルの材料選定に特に注意を払った。予備実験により、白金 (Pt) は 1473K まで Na 化合物との良い化学的適合性を確認できたので、この材質でセルを製作することとした。

信頼性のある測定システムであることを保証するために、Na を試料とした予備測定をはじめに実施した。Na の飽和蒸気圧は、390K から 470K の範囲で測定し、満足のいく精度の蒸気圧測定結果が得られた。

この予備試験を踏まえて、 $\text{Na}_4\text{FeO}_3(\text{s}) \rightarrow \text{Na}_3\text{FeO}_3(\text{s}) + \text{Na}(\text{g})$  の分解反応について、高温質量分析計を用いた研究を実施した。Na 蒸気圧の温度依存性については、590K から 717K の温度範囲で、 $P_{\text{Na}}/P_{\text{a}} = 3.8589 \times 10^{10} \exp(-17749/T)$  を得た。反応の熱力学関数は、以下のとおり得られた。

$$\Delta_r H^\circ(653\text{K}) = 148.5 \text{ kJ/mol}, \Delta_r G^\circ(T) = 148522 - 108.29 \times T.$$

$\text{Na}_4\text{FeO}_3$  の文献値を参考にして、 $\text{Na}_3\text{FeO}_3$  の生成ギブズエネルギーは、以下のように評価した。

$$\Delta_f G^\circ(\text{Na}_3\text{FeO}_3) = -1168629 + 338.34 \times T.$$

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# Determination of Gibbs Energy of Formation of $\text{Na}_3\text{FeO}_3$ by High Temperature Mass Spectrometer

## 1. Introduction

Thermodynamics of Na-Fe-O is one of the toughest topics in ternary systems. Since 1950s, a lot of research works have been done on sodium-iron oxides, such as  $\text{NaFeO}_2$ ,  $\text{Na}_4\text{FeO}_3$ ,  $\text{Na}_5\text{FeO}_4$ ,  $\text{Na}_3\text{FeO}_3$  and perhaps  $\text{Na}_2\text{FeO}_2$ . In 1951, King probably was the first researcher who measured the heat capacity and entropy of  $\text{Na}_2\text{Fe}_2\text{O}_4$ <sup>[1]</sup>(probably the same as  $\text{NaFeO}_2$ ). In 1961, Koehler et al. studied heat of formation of  $\alpha$ - $\text{NaFeO}_2$ ,  $\beta$ - $\text{NaFeO}_2$  and  $\gamma$ - $\text{NaFeO}_2$  by calorimetric measurement<sup>[2]</sup> while Watanabe reported crystal structure of  $\beta$ - $\text{NaFeO}_2$ <sup>[3]</sup>. In 1984 Dai et al. tried to measure the standard Gibbs energy of  $\text{NaFeO}_2$ <sup>[4-5]</sup> but their results were suspected by themselves about 10 years later<sup>[6]</sup>. There is large disagreement even for the melting point and phase transformation temperatures, so Ono et al. reexamined the phase transformations between  $\alpha$ - $\text{NaFeO}_2$  and  $\beta$ - $\text{NaFeO}_2$  at high temperatures by TG-DTA and DSC thermal analysis. They confirmed that phase transition from  $\alpha$ - $\text{NaFeO}_2$  to  $\beta$ - $\text{NaFeO}_2$  is irreversible<sup>[7]</sup>. Till now, only thermodynamic data of  $\text{NaFeO}_2$  was formally accepted by the Scientific Group Thermodata Europe(SGTE) among these ternary compounds<sup>[8-9]</sup>. Lindemer once evaluated thermodynamics for most of the Na-Fe-O compounds so that these evaluated data were widely used in 1980s<sup>[10]</sup>. However, Lindemer himself and some other researchers felt hard to explain some experimental results found later. A lot of efforts were paid to investigate these compounds. For example,  $\text{Na}_4\text{FeO}_3$  had been studied extensively from 1970 to 1997 but careful evaluation is still in need to compare the results reported by different laboratories as summarized in Table 1.

After the sodium-leaking incident at the Monju Fast Breeder Reactor in December 1995, attempts to understand more about these sodium-iron oxides were ignited once again. One India group continued to work on this topic and investigated the thermodynamic stability of Na-Fe-O system<sup>[16-17]</sup>. On behalf of JNC, the Swedish Kungl Tekniska Högskolan(KTH) tried again to obtain thermodynamics data by using vapor pressure measurement method. Unfortunately, there are some serious concerns about their experimental results and conclusions. As a result, a Knudsen effusion mass

spectrometer was constructed in JNC to try to obtain reliable partial vapor pressures over these compounds.

In the present report, the chemical compatibility of sample container materials with various sodium compounds was tested first; the published data of  $\text{Na}_4\text{FeO}_3$  is evaluated; then sodium vapor pressure over pure sodium was measured to test reliability of the whole system; finally  $\text{Na}_3\text{FeO}_3$  is able to be determined based on vapor pressure measurements over reaction  $\text{Na}_4\text{FeO}_3(\text{s}) = \text{Na}_3\text{FeO}_3(\text{s}) + \text{Na}(\text{g})$  by high temperature mass spectrometry.

**Table 1:** Summary of  $\Delta_f G^\circ(\text{Na}_4\text{FeO}_3)$  in  $\text{J/mol} = A + B \times T (\text{K})$

Temperature	A	B	Error	Date	Ref.
400-1100K	-1160562.2	263.40	Not available	1993-1997 Thermo-Calc Database	Du, Dai Seetharaman Sweden [11]
371-904K	-1205503.3	347.28	Not available	1990 MALT2 database	Yokokawa Japan [12]
773-904K	-1168881.3	271.44	Not available	1989	Sridharan India [13]
723-873K	-1212202	351.10	$\pm 2100$	1988	Bhat Germany [14]
298.15K	-1211000	337.644	Not available	1981	Lindemer USA [10]
700-1100K	-1215000	342.46	$\pm 12600$	1977	Shaiu USA [15]

## 2. Chemical compatibility of the Knudsen cell with sodium compounds

After the sodium-leaking incident in FBR, many researches were carried out in JNC to predict its effects. Various experimental methods were employed to measure the properties of sodium compounds involved in the sodium-leak events, for example, by the high temperature X-ray diffraction, the TG-DTA and DSC thermal analysis, the

Raman analysis as well as mass spectrometric analysis. Among these experimental measurements, one common problem is the compatibility of sample container with the sodium compounds because sodium is chemically so active that even its compounds tend to react with container materials at high temperatures. Consequently, researchers have to carefully consider how to find a proper material that has little influence to the specimen and is easy to be made.

It is noticed by almost all the researchers that sodium might react with the Knudsen cell so that careful attentions must be paid to choose proper material for the Knudsen cell. Here is a brief summary of the researches. In 1970, Hildenbrand used beryllia as the cell but he changed to Pt-Rh cell when he reexamined the vaporization of  $\text{Na}_2\text{O}(\text{s})$  again in 1993<sup>[18-19]</sup>. In 1984, Hilpert used Mo and quartz glass to investigate vaporization of liquid sodium. According to his experiments, Mo is most likely to avoid possible reactions between sodium and the cell when oxygen potential is very negative<sup>[20]</sup>. Jayanthi used graphite to be his cell to measure  $\text{NaUO}_3$ <sup>[21]</sup>. To look for a specific material that has minimum influence on Na-Fe-O system, careful theoretic evaluation and experimental test were made in the next section.

## 2.1 Theoretic evaluation of candidate cell materials

Metal may be considered as the first candidate substance because it is easy to be processed and conjunct with other part of the equipment. In our Q-mass equipment, the sample is contained in the Knudsen cell that requires to be hermetically sealed except for an orifice with high precision to let the gases go out. So ceramics is not very suitable for the Knudsen cell, even it seems to have good resistance to the corrosion of sodium.  $\text{NaFeO}_2$  and  $\text{NaOH}$  were chosen to represent sodium compounds. The former represents sodium iron complex compounds such as  $\text{Na}_4\text{FeO}_3$ ,  $\text{Na}_3\text{FeO}_3$ , etc... while the later is expected to reflex the practical environmental condition when water vapor cannot be excluded.

At the beginning of the research, most of the metals wildly used in high temperature industry were theoretically evaluated for our own propose from fundamental considerations, such as melting points, ability to form oxides or hydroxides etc...as listed in Table 2. Firstly, Ag, In and Au can be excluded from the list because their melting points are not high enough. Secondly, Hf, V, Cr, Zr and Ti are likely to be oxidized easily since their corresponding enthalpies of formation are too low, say, less

than  $-1000$  kJ/mol. Thirdly, W, Mo, Mn, Co, Ta and Nb are not proper either due to possible formation of their complex oxides. Finally, Pt is selected from the left possible candidates of Pt, Pd, Re and Ir, since Pt is well utilized as high temperature noble materials for further test.

Table 2: Properties of corresponding metals and compounds

Metal	Melting Point °C	Metal oxides	$\Delta_f H^\circ$ (kJ/mol)	Sodium complex compounds	$\Delta_f H^\circ$ (kJ/mol)	Hydroxide at 1000K	$\Delta_f H^\circ$ (kJ/mol)
W	3422	WO <sub>2</sub>	-589	Na <sub>2</sub> WO <sub>4</sub>	-1542	W(OH)(gas)	-435
Re	3186	ReO <sub>2</sub>	-432	NaReO <sub>4</sub>	Formed at High Pres.		
Ta	3020	TaO <sub>2</sub>	-184	Na <sub>3</sub> TaO <sub>4</sub>			
Mo	2623	MoO <sub>2</sub>	-588	Na <sub>2</sub> MoO <sub>4</sub>	-1534	Mo(OH) <sub>2</sub> (gas)	-3.3
Nb	2469	NbO <sub>2</sub>	-795	Na <sub>3</sub> NbO <sub>4</sub>			
Ir	2447	IrO <sub>2</sub>	-249				
Hf	2231	HfO <sub>2</sub>	-1117				
V	1910	V <sub>2</sub> O <sub>3</sub>	-1218	NaVO <sub>2</sub>			
Cr	1863	Cr <sub>2</sub> O <sub>3</sub>	-1135	NaCrO <sub>2</sub>		Cr(OH) <sub>2</sub> (gas)	-274
Zr	1855	ZrO <sub>2</sub>	-1100	Na <sub>2</sub> ZrO <sub>3</sub>			
Pt	1769			NaPt <sub>3</sub> O <sub>4</sub> Na <sub>2</sub> PtH <sub>6</sub> NaPt <sub>2</sub>	Formed at High Pres.		
Ti	1670	Ti <sub>2</sub> O <sub>3</sub>	-1521	Na <sub>2</sub> TiO <sub>3</sub>			
Pd	1555	PdO	-115				
Fe	1538	Fe <sub>2</sub> O <sub>3</sub>	-823	Target		Fe(OH) <sub>2</sub> (gas)	-238
Co	1495	CoO	-238	Na <sub>x</sub> CoO <sub>2</sub>		Co(OH) <sub>2</sub> (s)	-541
Ni	1455	NiO	-240	Na <sub>2</sub> NiO <sub>2</sub>	700-800°C	Ni(OH) <sub>2</sub> (s)	-532
Mn	1246	MnO	-385	Na(MnFe)O <sub>2</sub>		Mn(OH) <sub>2</sub> (s)	-696
Au	1064	Au <sub>2</sub> O <sub>3</sub>	-3.4			Au(OH) <sub>3</sub> (s)	-308
Ag	960	Ag <sub>2</sub> O	-31.1				
In	156	In <sub>2</sub> O <sub>3</sub>	-926	NaInO <sub>2</sub>		InOH(gas)	-88

Note: Most of the thermodynamic data were from Ref. [22] and Ref. 27-37.

## 2.2 Experiments on some candidate cell materials

The first Knudsen cell in our Q-mass equipment was made of molybdenum referred to Ref.[20]. So the test was first made on Mo-Na-O-H system. Then other tests in Pt-Na-O-H were done as Pt is recommended as the best candidate material in the previous section.

### ● Test of Mo as cell material

Chemical compatibility of Mo with  $\text{NaFeO}_2$  and  $\text{NaOH}$  were tested separately at high temperatures. The results are discussed here.

#### (1) $\text{NaFeO}_2$ in Mo-cell

One piece of Mo sample cell was inserted into the  $\text{NaFeO}_2$  powder and heated from room temperature to 1473 K. The whole process was viewed by an optical microscope and recorded in videotapes. It seemed that Mo-cell remained its apparent shape and no significant evidence of severe reaction was observed as shown in Fig. 1-3.

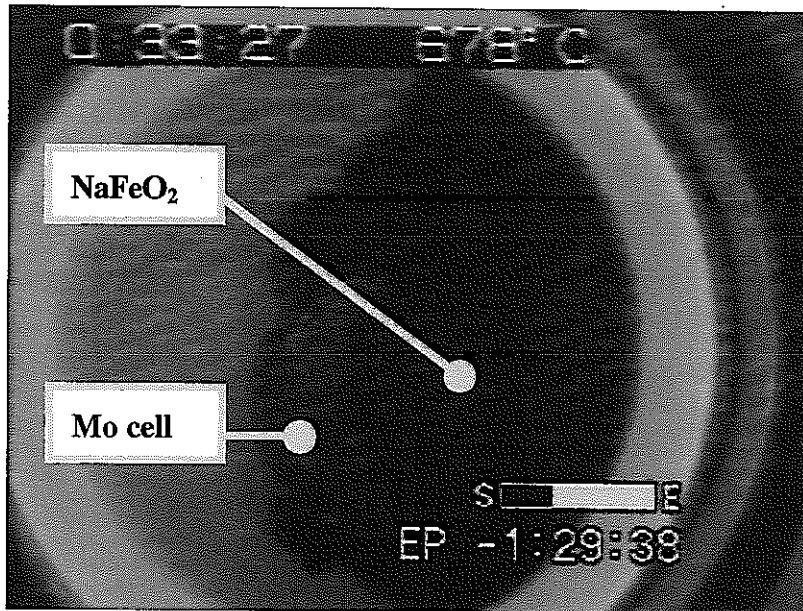


Figure 1: Optical view of Mo+ $\text{NaFeO}_2$  at 951 K

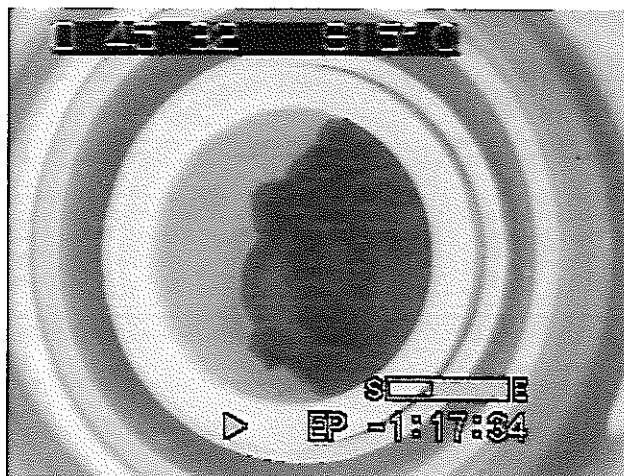


Figure 2: Optical view of Mo-cell with NaFeO<sub>2</sub> at 1188 K



Figure 3: Optical view of Mo-cell with NaFeO<sub>2</sub> at 1472 K

After the heating experiment, however, some sodium molybdenum oxides were identified by X-ray powder diffraction. Na<sub>2</sub>MoO<sub>4</sub> was found inside the source materials of NaFeO<sub>2</sub> (Fig.4).

Repeat test was also done on a real Mo Knudsen cell with NaFeO<sub>2</sub> inside. A film of Na<sub>2</sub>Mo<sub>3</sub>O<sub>6</sub> was found deposited on the inner surface of cover of Mo Knudsen cell (Fig. 5). Therefore, if Mo cell were used as the Knudsen cell, it would greatly affect the equilibrium state and cause confusion for the analysis by the Q-mass vaporization measurements.

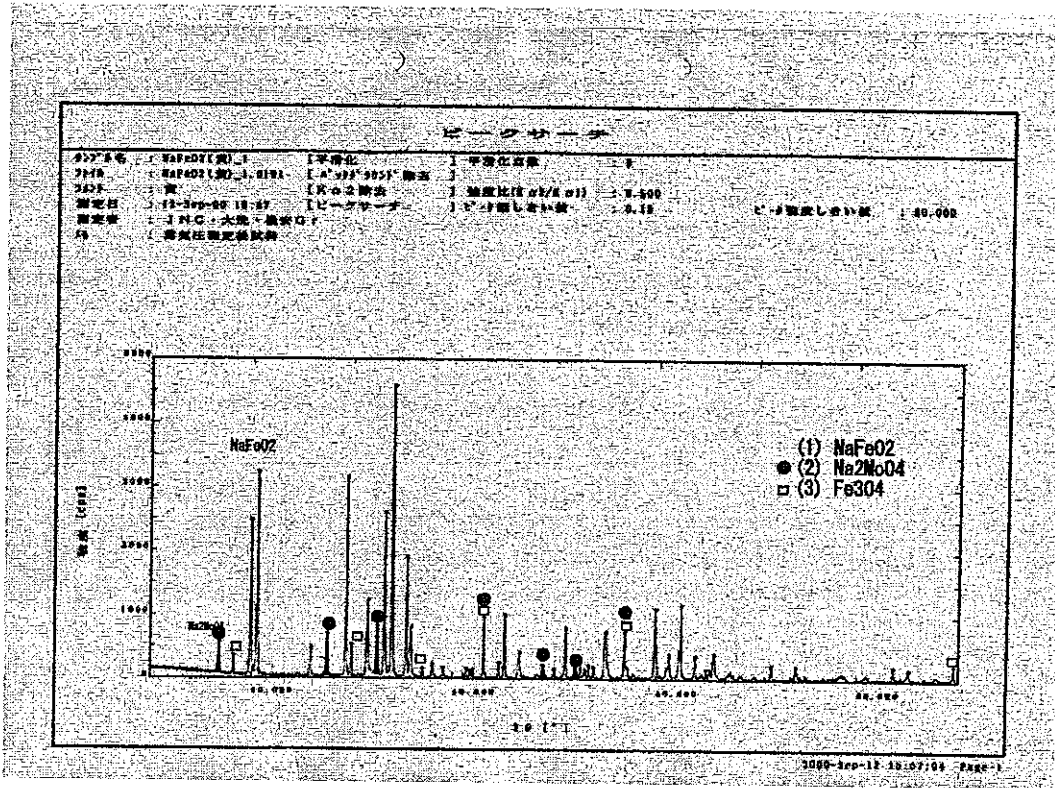


Figure 4: X-ray powder diffraction pattern after NaFeO<sub>2</sub>+Mo being heated up to 1473 K

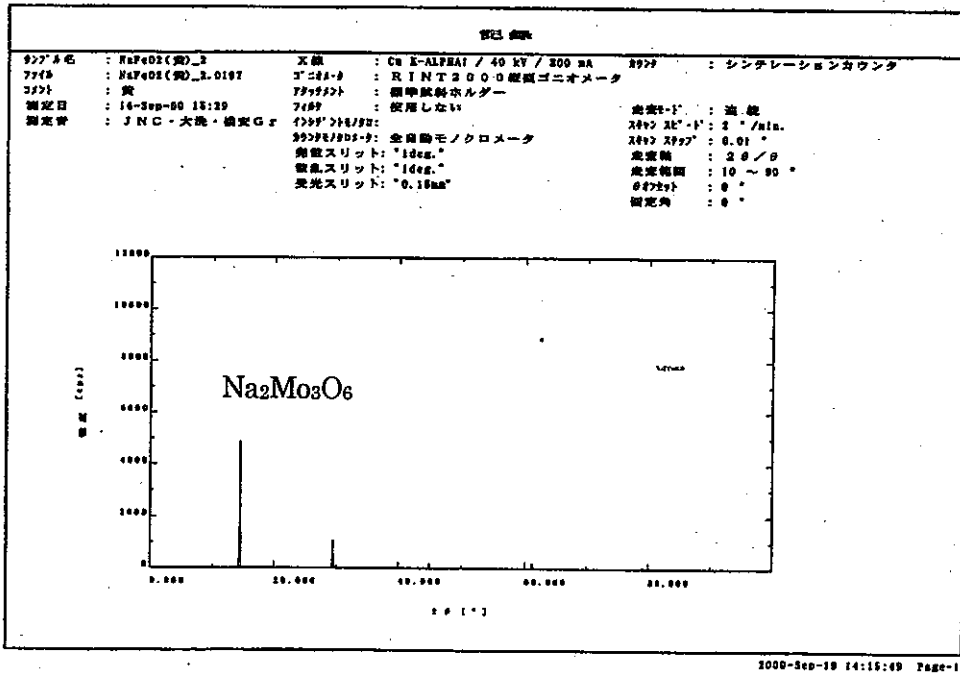


Figure 5: X-ray powder diffraction pattern of the inner surface of Mo Knudsen cover after being tested with NaFeO<sub>2</sub> up to 1473 K.

(2) NaOH and Mo

When NaOH was put together with a Mo sample plate and heated up. Severe reaction occurs between them. Mo plate became very fragile after the test and was easily broken into pieces as shown in Fig. 6-9.



Figure 6: Optical view of Mo with NaOH at about 733 K when NaOH melts

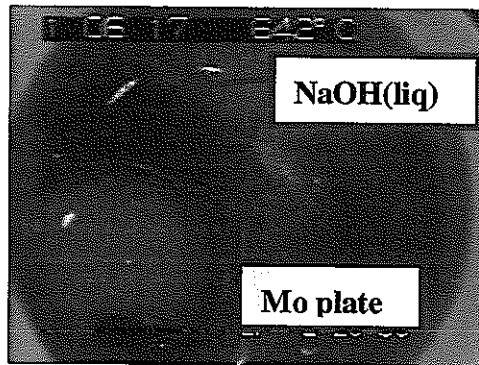


Figure 7: Optical view of Mo with NaOH at 915 K



Figure 8: Optical view of Mo with NaOH at 1018 K when NaOH is almost completely evaporated



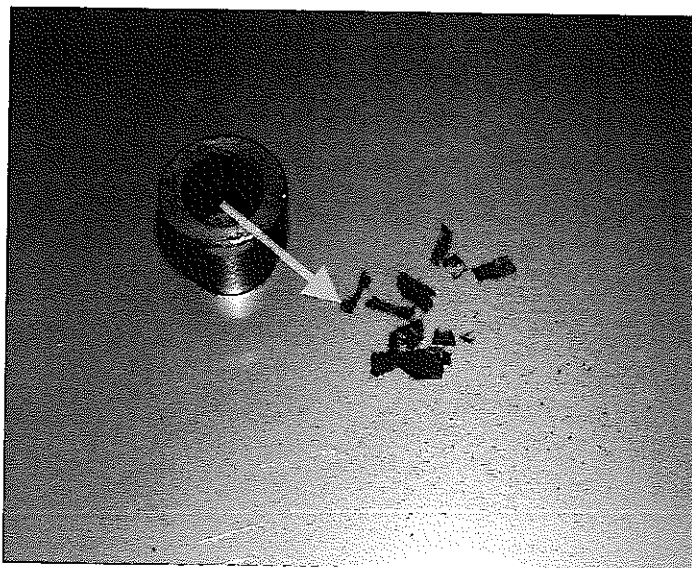


Figure 9: A Mo Knudsen cell breaks into pieces after reaction with NaOH

Physical examination showed the terrible damage of Mo cell after NaOH test. So, Mo is obviously not suitable for this purpose even the temperature is not very high.

● **Test of Pt as cell material**

Chemical compatibilities of platinum with  $\text{NaFeO}_2$ , NaOH as well as a mixture of  $\text{Na}_2\text{O}+\text{Na}_2\text{O}_2$  were tested, respectively.

(1)  $\text{NaFeO}_2$  in Pt

No chemical reactions between sample Pt film and  $\text{NaFeO}_2$  powder were observed as shown in Fig. 10-12. The Pt film is in perfect condition even over 1473 K when  $\text{NaFeO}_2$  starts to melt (Fig. 10). There were no other compounds that could be identified except for the source material  $\text{NaFeO}_2$  and its decomposition product  $\text{Fe}_3\text{O}_4$ . It indicates that platinum can stay well with sodium without damage till 1473 K. It should be noted that other researchers found evidence of corrosion on Pt when temperature is about 1523 K<sup>[7]</sup>. When temperature is over 1473 K, Pt is not recommended to use together with Na.

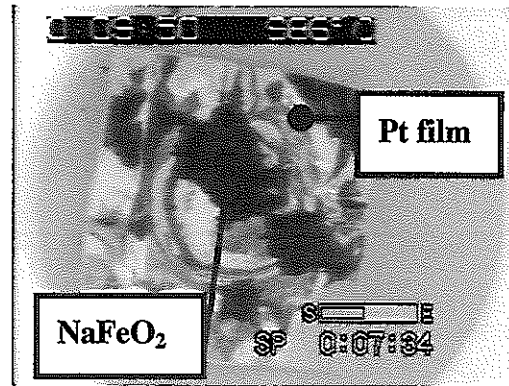


Figure 10: Optical view of Pt film with NaFeO<sub>2</sub> at 1259 K

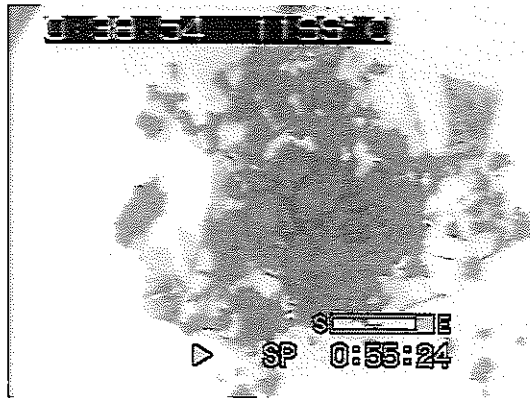


Figure 11: Optical view of Pt film with NaFeO<sub>2</sub> at 1472 K



Figure 12: Optical view of Pt film with NaFeO<sub>2</sub> when NaFeO<sub>2</sub> melts

Note: The temperature was actually much higher than 1473 K because of a pulse heating.

(2) NaOH in Pt-cell

A cell made of Pt remained unchanged even when all the liquid NaOH was evaporated completely around 1233 K as shown in Fig. 13-15. A practical test in Pt Knudsen cell in the Q-mass experiment also showed the same result (Fig. 16).

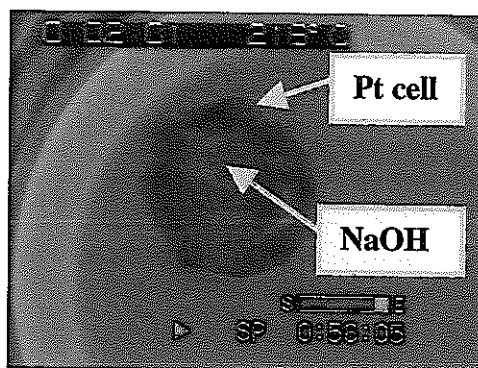


Figure 13: NaOH in Pt-cell at 491 K before NaOH melts

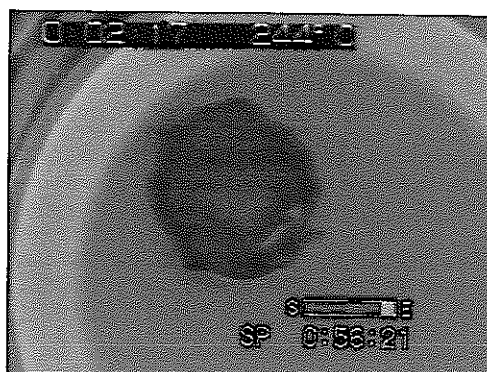


Figure 14: NaOH in Pt-cell at 517 K after NaOH melts



Figure 15: Pt-cell at 1233 K after NaOH has been completely evaporated



Figure 16: Pt-cell remains perfect after being heated with NaOH up to 1273 K

The composition change of the sample was analyzed by X-ray powder diffraction. Only the  $\text{Fe}_3\text{O}_4$  and  $\text{NaFeO}_2$  were found after the test as shown in Fig. 17-18. No other compounds between Pt and Na or oxygen were found. It means that Pt did not react with Na or oxygen in this test condition.

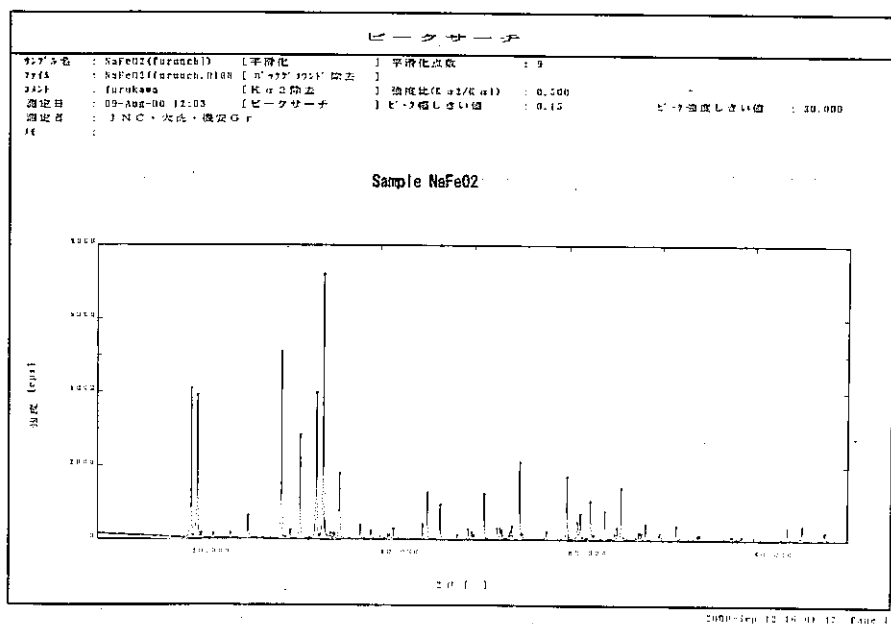


Figure 17: X-ray diffraction pattern of the  $\text{NaFeO}_2$  sample before it is heated in Pt cell

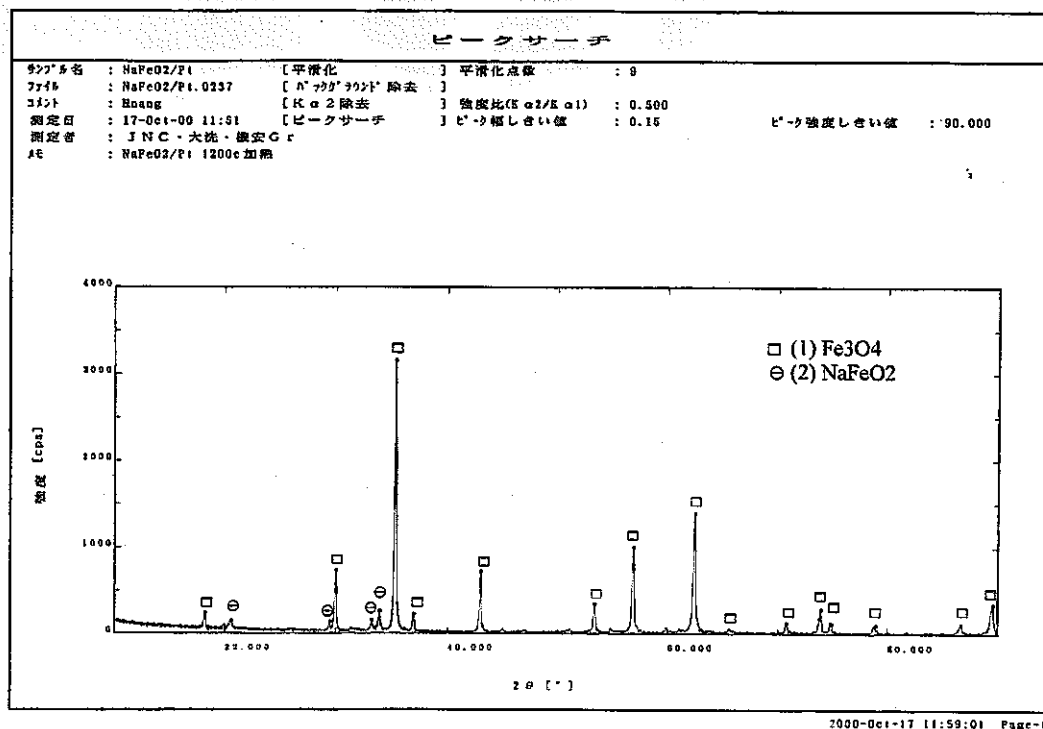


Figure 18: X-ray diffraction pattern of the NaFeO<sub>2</sub> sample after being heated in Pt cell

(3) 95%Na<sub>2</sub>O + 5%Na<sub>2</sub>O<sub>2</sub> in Pt-cell

This mixture was selected to test the chemical stability of platinum because the mixture has relatively higher oxygen potential. The test results show that Pt cell is a little oxidized but still good enough for the present research (Fig. 19).

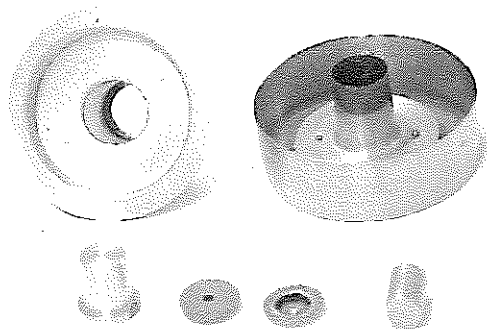


Figure 19: The Pt-cell and its surrounding parts made of Pt after the high temperature test

In summary, Mo is not a good material to make Knudsen cell. Pt shows very good chemical compatibility with sodium compounds, no matter with sodium or NaOH, as long as the temperature is not higher than 1473 K. So, Pt is determined to be the Knudsen cell material and is experimentally proved to be stable and has little influence on sodium compounds.

### 3. Evaluation of thermodynamic data of $\text{Na}_4\text{FeO}_3$

To get reliable data of  $\text{Na}_3\text{FeO}_3$ , the thermodynamic data of  $\text{Na}_4\text{FeO}_3$  is necessary because decompose reaction  $\text{Na}_4\text{FeO}_3(\text{s}) = \text{Na}_3\text{FeO}_3(\text{s}) + \text{Na}(\text{gas})$  is involved in the present case (The detail will be discussed later in section 5.2. ). Up to now, about 8 references can be found in which the thermodynamic data of  $\text{Na}_4\text{FeO}_3$  was either experimentally determined or theoretically estimated as listed in Table 3 and shown in Fig. 20 also. The purpose now is to make a whole evaluation on these data and try to find the best data of highest reliability.

Table 3: Thermodynamic values of  $\text{Na}_4\text{FeO}_3$  published in references

No.	Authors	Method	Temperature (K)	$\Delta_f G^\circ(\text{Na}_4\text{FeO}_3) = \Delta H^\circ + \Delta S^\circ \times T$	Error
(1)	Ref.[6], KTH, Sweden Du & Seetharaman (1993-1997)	Evaluation		$\Delta H^\circ = -1099575$ $\Delta S^\circ = 256.77$	Not available
(2)	Ref.[12] MALT2, 1991.	Evaluation		$\Delta H^\circ = -1195746$ $\Delta S^\circ = 320.10$	Not available
(3)	Ref.[13] Sridharan India, 1989	Experiment	773-904	$\Delta H^\circ = -1168881.3$ $\Delta S^\circ = 271.44$	Not available
(4)	Ref.[14], Bhat Germany, 1988	Experiment	723-873	$\Delta H^\circ = -1212202$ $\Delta S^\circ = 351.10$	$\pm 2100$
(5)	Ref.[10], Lindemer USA, 1981	Evaluation		$\Delta H^\circ = -1211000$ $\Delta S^\circ = 337.644$	
(6)	Ref.[15], Shaiu USA, 1977	Experiment	700-1100	$\Delta H^\circ = -1215000$ $\Delta S^\circ = 342.46$	$\pm 12600$
(7)	Ref.[26] Gross, Wilson USA, 1970	Experiment $2\text{Na}_2\text{O} + \text{FeO} = \text{Na}_4\text{FeO}_3$ $\Delta_r H^\circ(298) = -104893 \pm 2300$	298.15	$\Delta H^\circ = -1212841^*$	$\pm 2300$
(8)	Ref.[5], KTH, Sweden, Dai, 1984	Experiment $2\text{Na}_2\text{O} + \text{FeO} = \text{Na}_4\text{FeO}_3$ $\Delta_r H^\circ(298) = -147988 \pm 8200$	298.15	$\Delta H^\circ = -1255936^*$	$\pm 8200$

\* Note: reproduced by the present author by assuming  $\Delta_f H^\circ(298.15\text{K}) = \Delta_f H^\circ(T) - 4000$

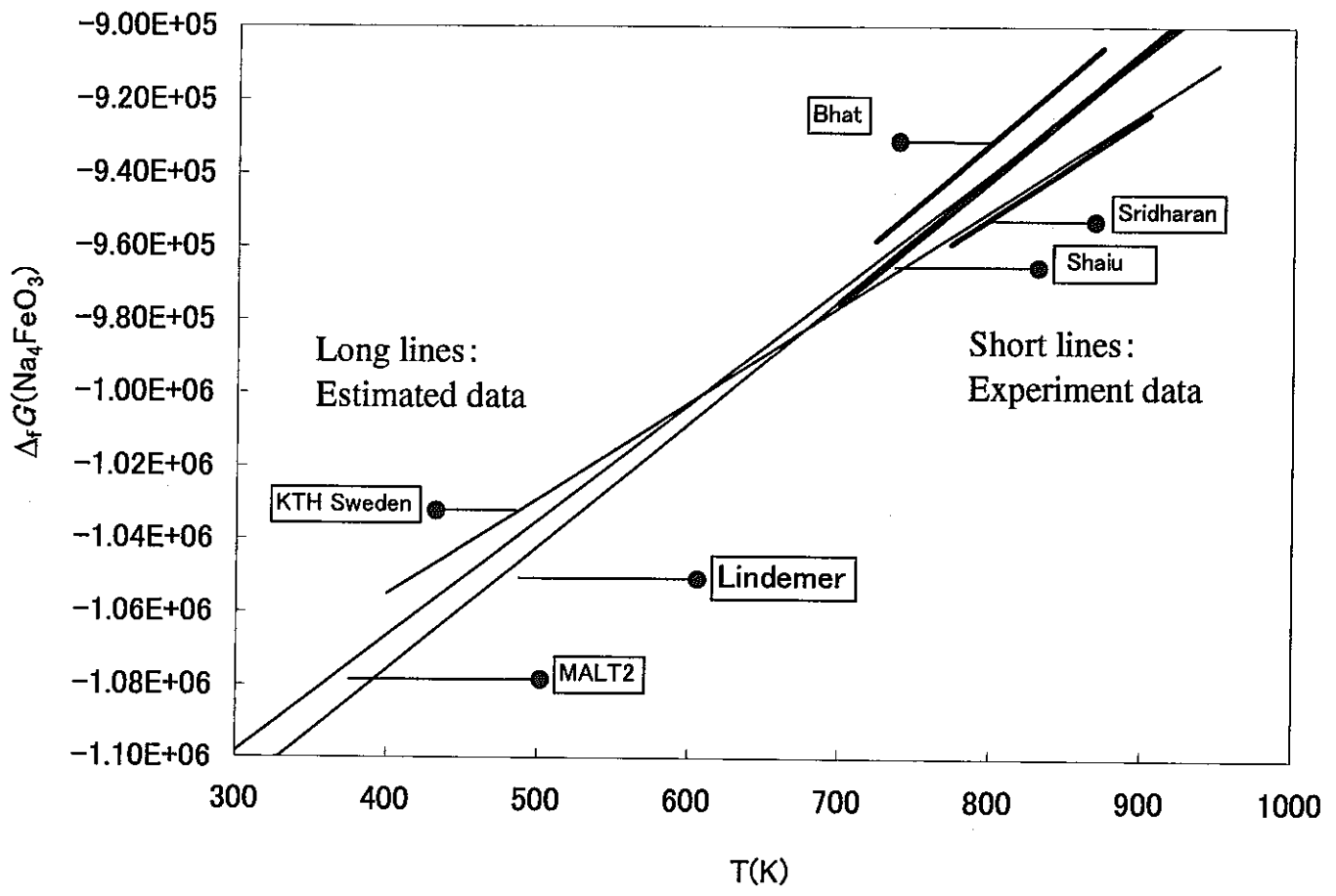


Figure 20: Comparison of  $\Delta_f G^\circ(\text{Na}_4\text{FeO}_3)$  values from references



As for the Gibbs energy of formation of  $\text{Na}_4\text{FeO}_3$ , the equation can be expressed as,

$$\Delta_f G^\circ(\text{Na}_4\text{FeO}_3) = \Delta H^\circ - \Delta S^\circ \times T \text{-----} (1)$$

From Table 3, we can find that 3 experimental data of  $\Delta H^\circ(\text{Na}_4\text{FeO}_3)$  are close to each other, i.e.,  $-1212.2$  kJ/mol by Bhat (1988),  $-1215$  kJ/mol by Shaiu (1977) and  $-1217$  kJ/mol by Gross (1970). There is only 0.4% difference among these values.

On the other hand, Dai got  $\Delta H^\circ = -1256$  kJ/mol in 1984 but he rejected this data and modified it to be  $-1100$  kJ/mol about 10 years later. In 1989, an Indian researcher Sridaran reported  $\Delta H^\circ = -1169$  kJ/mol but he also admitted there was some uncertainty in his system and the data may only be taken as a reference.

Lindemer and MALT2 database both gave their theoretical evaluations on this value. Their values are  $-1211$  kJ/mol and  $-1196$  kJ/mol, respectively.

Considering the precision given by Bhat was the best among the 3 experimental results, his result is employed in this study, i.e,

$$\Delta_f G^\circ(\text{Na}_4\text{FeO}_3) \pm 2100 \text{ J/mol} = -1212202 - 351.10 \times T \text{-----} (2)$$

#### 4. Pressure calibration by pure sodium

According to a few times preliminary testing measurements on sodium iron oxides, the measuring temperature range of mass spectrometer is about 573 to 973 K because the total vapor pressure over sodium iron oxides cannot go over a few Pascal. Therefore, calibration by silver or Pb is no longer very suitable for this situation because they are usually used to calibrate at higher temperature range such as over 1173 K or higher temperatures.

On the other hand, sodium is found to be the most abundant vapor species over sodium iron oxides at high temperatures. So pure sodium was employed as a standard

reference to testify reliability of the whole high temperature mass spectrometric system, since its partial vapor pressure has been well investigated and reliable data are given in many literatures.

Saturated vapor pressure of sodium is measured (390-470K) in the present experiment and can be expressed as,

$$P \text{ (Pa)} = \exp(-171.2 - 2335/T + 28.03 \ln(T)) \text{ ----- (3)}$$

It agrees well with the ANL's values<sup>[38]</sup> extrapolated from the higher temperature range (800-2500K) as shown in Fig. 20.

The reaction enthalpy of Na(liq.)=Na(gas) at 430K, the mean temperature of the measurement range, is calculated as the following.

$$\Delta_r H^\circ (430\text{K}) = -R \frac{d \ln P_{\text{Na}}}{d(1/T)} = 101.1 \pm 4.4 \text{ (kJ/mol) ----- (4)}$$

Comparison with ANL extrapolated data  
Na(Liq.)=Na(Gas)

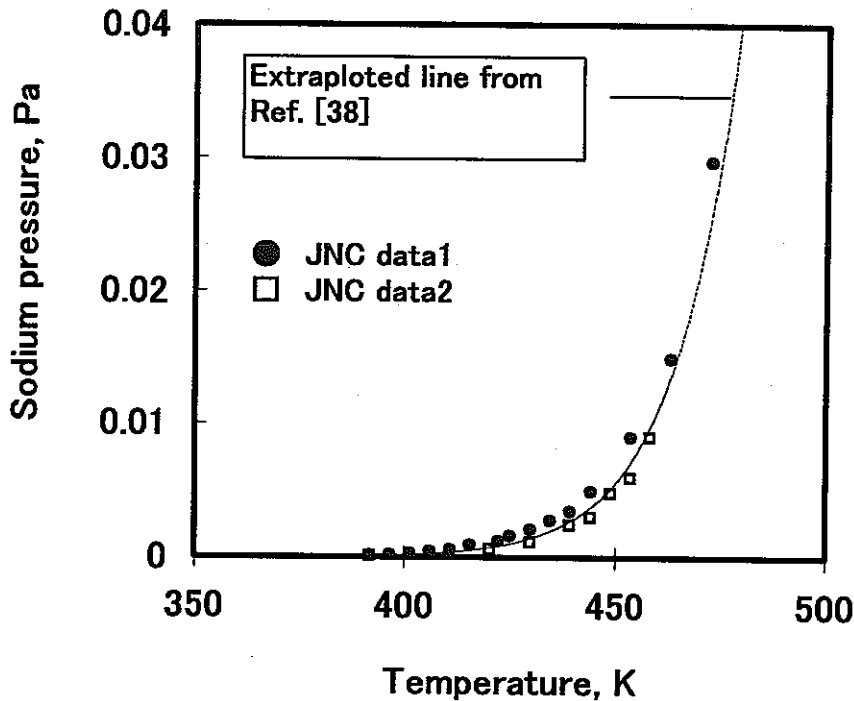


Figure 21: Saturated vapor pressure of sodium

It is close to 103.6 kJ/mol given by Thermo-Calc database. The standard enthalpy of formation of sodium gas can also be calculated from the vapor pressure measurement results.

$$\Delta_f H^\circ(298.15\text{K})=105.0\pm 4.4 \text{ kJ/mol (by the 2nd law treatment),}$$

$$\Delta_f H^\circ(298.15\text{K}) = 107.6\pm 0.8 \text{ kJ/mol (by the 3rd law treatment).}$$

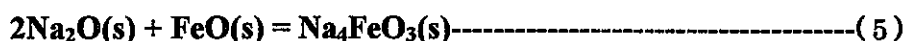
They agree well with the 107.3 kJ/mol given by the Thermo-Calc database. This also shows the good precision of the high temperature mass spectrometer used in the present study. Then, the calibration factor K is determined from the above results and is used to calculate partial vapor pressures in the following chapters.

## 5. Vaporization behavior of $\text{Na}_4\text{FeO}_3$

High temperature mass spectrometric study was carried out from 590 to 717 K. The electron impact energy is set to be 9.8eV. The emission current is 0.1mA. The Secondly Electron Multiplier factor is set to be 1000, so that weak signal can be measured also.

### 5.1 Sample identification

Pure  $\text{Na}_4\text{FeO}_3$  was installed in the Pt-cell for the high temperature mass spectrometric experiments. Though the manufacture process of  $\text{Na}_4\text{FeO}_3$  has been described by T. Furukawa et al in detail<sup>[7]</sup>, a brief introduction is given here for reader's convenience. Purified  $\text{Na}_2\text{O}$  and  $\text{FeO}$  were mixed with molar ratio of 2:1 and kept at 873 K for 100 hours.



Pure  $\text{Na}_4\text{FeO}_3$  was successfully obtained in this way. X-ray powder diffraction analysis identified the sample prepared was almost single phase  $\text{Na}_4\text{FeO}_3$ (Fig. 22).

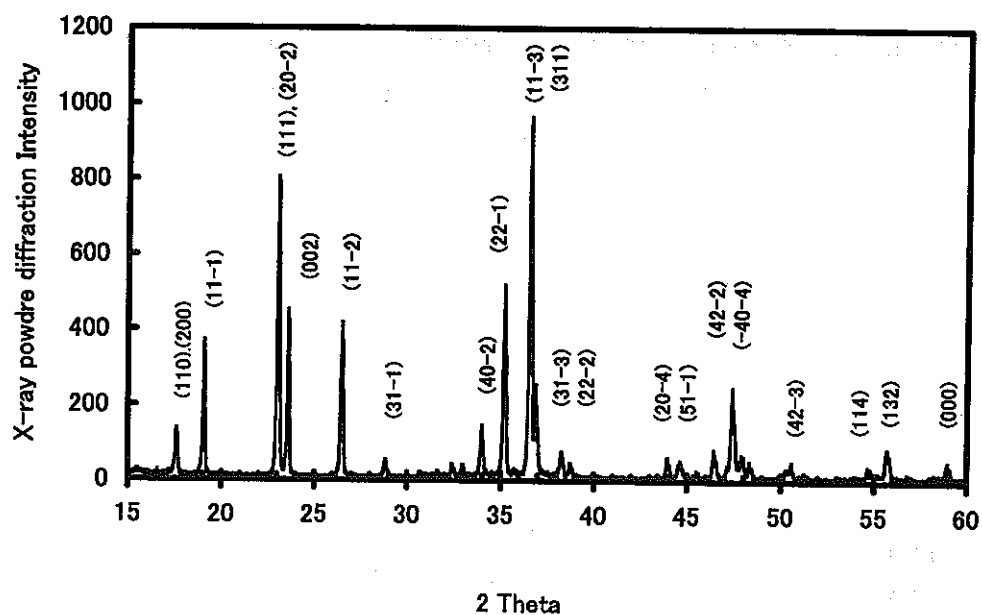


Figure 22: X-ray powder diffraction pattern of  $\text{Na}_4\text{FeO}_3$  sample prepared for the high temperature mass spectrometric measurements

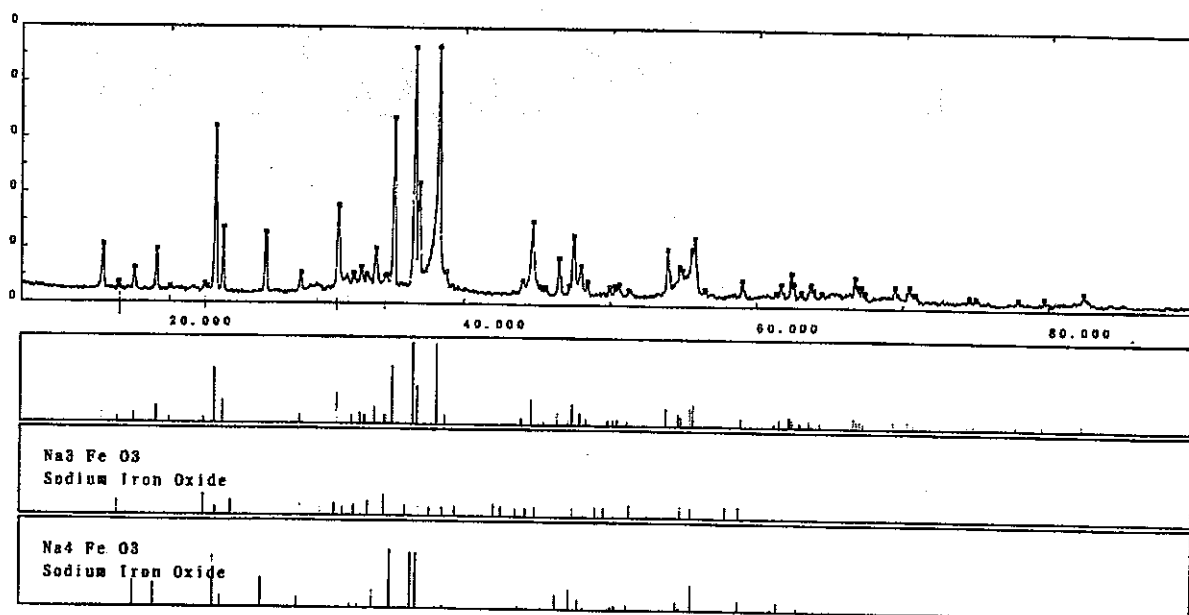


Figure 23: X-ray powder diffraction pattern of the testing materials after  $\text{Na}_4\text{FeO}_3$  sample was heated at about 673 K for about 4 hours in the high temperature mass spectrometer

After  $\text{Na}_4\text{FeO}_3$  was heated at about 673 K, the specimen was taken out to do X-ray powder diffraction analysis. At this stage,  $\text{Na}_4\text{FeO}_3$  and  $\text{Na}_3\text{FeO}_3$  were both found as shown in Fig. 23. A rough comparison indicated that  $\text{Na}_4\text{FeO}_3 : \text{Na}_3\text{FeO}_3 = 9 : 1$ . Another experiment for about 30 hours in the high temperature mass spectrometer resulted in complete decomposition of  $\text{Na}_4\text{FeO}_3$ . The product was identified as almost pure  $\text{Na}_3\text{FeO}_3$  as shown in Fig. 24. A trace amount of  $\text{NaOH}$  was found but it should be attributed to the environmental influence when the sample was transferred into X-ray sampling room in atmosphere in which water vapor must be absorbed into the sample surface.

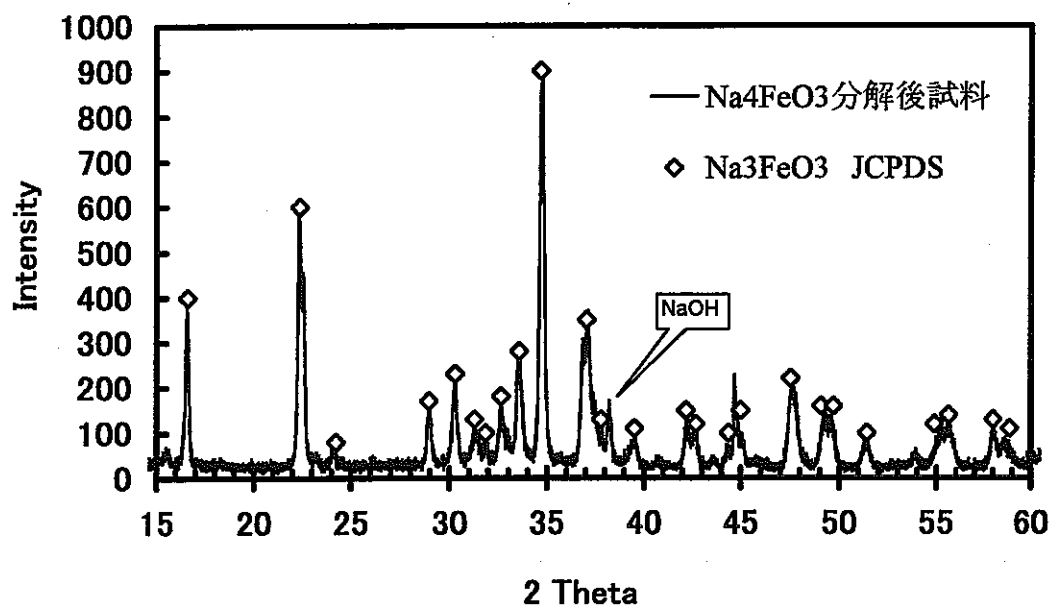


Figure 24: X-ray powder diffraction pattern of the testing materials after  $\text{Na}_4\text{FeO}_3$  sample was heated for about 30 hours in the high temperature mass spectrometer

## 5.2 Vapor pressure measurement over $\text{Na}_4\text{FeO}_3(\text{s})$

$\text{Na}(\text{g})$  was found as the main vapor species over  $\text{Na}_4\text{FeO}_3$ . Dimmer  $\text{Na}_2(\text{g})$  was also found but its intensity was measured to be about 3-4 orders of magnitude lower than that of the monomer. Other possible vapor species such as  $\text{NaO}(\text{g})$  and  $\text{Na}_2\text{O}(\text{g})$  were unable to be distinguished from the background probably caused by rotary pump oil.

According to the sample identification results as described in the previous section, the following reaction was assumed to occur inside the Knudsen cell,

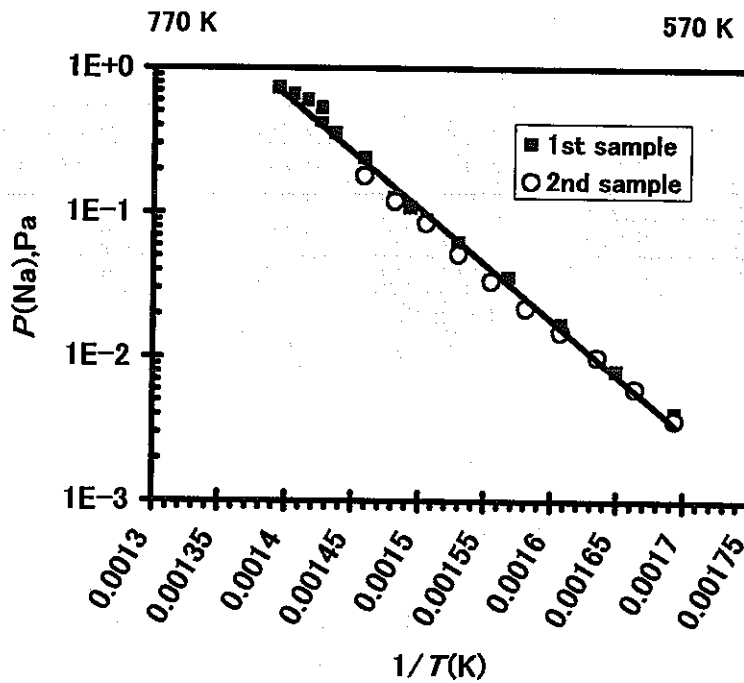
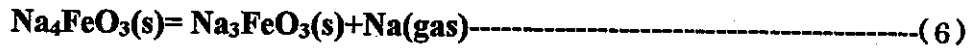


Figure 25: Sodium vapor pressure over Na<sub>4</sub>FeO<sub>3</sub>(s)

To acquire reliable data, two specimen of Na<sub>4</sub>FeO<sub>3</sub> were measured separately. The temperature dependence of sodium pressure over Na<sub>4</sub>FeO<sub>3</sub> was plotted in Fig. 25. It shows that two samples produced very consistent results.

In the temperature range from 590 to 717 K, the partial vapor pressure of sodium can be expressed as,

$$P_{\text{Na}}/\text{Pa} = 3.8589 \times 10^{10} \exp(-17749/T) \text{-----} (7)$$

Or,

$$\ln(P_{\text{Na}}) = 24.376 - \frac{17749}{T} \text{-----} (8)$$

## 6. Determination of the Gibbs energy of formation of $\text{Na}_3\text{FeO}_3$

Based on the present experiment measurement, thermodynamic functions related to the decomposition reaction (6) were calculated from about 26 experimental points as listed in Table 4.

Table 4: The reaction Gibbs energy change  $\Delta_r G^\circ(T)$  and equilibrium constant  $K_p(T)$

$T(^{\circ}\text{C})$	$T(\text{K})$	$P(\text{Na}), \text{Pa}$	$\Delta_r G^\circ = -RT \ln P$	$K_p$	$\Delta_r S$
317.4	590.55	4.10E-03	8.36E+04	4.05E-08	108.9
333.27	606.42	8.09E-03	8.24E+04	7.99E-08	108.0
349.14	622.29	1.69E-02	8.07E+04	1.67E-07	107.9
365.01	638.16	3.58E-02	7.88E+04	3.54E-07	108.2
380.88	654.03	6.25E-02	7.78E+04	6.17E-07	107.2
391.46	664.61	8.91E-02	7.71E+04	8.79E-07	106.6
396.75	669.9	1.09E-01	7.66E+04	1.07E-06	106.5
402.04	675.19	1.27E-01	7.63E+04	1.25E-06	106.1
412.62	685.77	2.40E-01	7.39E+04	2.37E-06	107.9
423.2	696.35	3.53E-01	7.28E+04	3.49E-06	107.9
428.49	701.64	4.31E-01	7.21E+04	4.25E-06	107.9
428.49	701.64	5.31E-01	7.09E+04	5.24E-06	109.7
433.78	706.93	6.00E-01	7.07E+04	5.92E-06	109.1
439.07	712.22	6.57E-01	7.07E+04	6.49E-06	108.3
444.36	717.51	7.27E-01	7.07E+04	7.17E-06	107.6
317.4	590.55	3.68E-03	8.41E+04	3.63E-08	108.0
327.98	601.13	6.13E-03	8.31E+04	6.05E-08	107.8
338.56	611.71	1.01E-02	8.20E+04	9.95E-08	107.7
349.14	622.29	1.49E-02	8.14E+04	1.47E-07	106.9
359.72	632.87	2.19E-02	8.07E+04	2.17E-07	106.1
370.3	643.45	3.35E-02	7.98E+04	3.30E-07	105.8
380.88	654.03	5.19E-02	7.88E+04	5.12E-07	105.7
391.46	664.61	8.50E-02	7.73E+04	8.39E-07	106.2
402.04	675.19	1.20E-01	7.66E+04	1.18E-06	105.6
412.62	685.77	1.80E-01	7.55E+04	1.78E-06	105.6

From the second law treatment, thermodynamic change of the reaction (6) can be obtained at the mean temperature of the measurements.

$$\Delta_r H^\circ(653 \text{ K}) = 148522.2 \pm 2753.8 \quad (\text{J/mol})$$

$$\Delta_r S^\circ(653 \text{ K}) = 108.29 \pm 4.18 \quad (\text{J/mol.K})$$

$$\Delta_r G^\circ(T) = (148522.2 \pm 2753.8) - (108.29 \pm 4.18) \times T \quad (590-717 \text{ K}) \text{ -----(9)}$$

From the decomposition reaction (6), it is easy to derive that

$$\Delta_f G^\circ(T) = \Delta_f G^\circ(\text{Na}_3\text{FeO}_3) + \Delta_f G^\circ(\text{Na, gas}) - \Delta_f G^\circ(\text{Na}_4\text{FeO}_3). \text{-----}(10)$$

So,

$$\Delta_f G^\circ(\text{Na}_3\text{FeO}_3) = \Delta_f G^\circ(T) - \Delta_f G^\circ(\text{Na, gas}) + \Delta_f G^\circ(\text{Na}_4\text{FeO}_3). \text{-----}(11)$$

From SGTE database given by Thermo-Calc, the Gibbs energy of formation of Na(gas) can be expressed as,

$$\Delta_f G^\circ(\text{Na, gas}) = 104949 - 95.53 \times T. \text{-----}(12)$$

While,

$$\Delta_f G^\circ(\text{Na}_4\text{FeO}_3) = -1212202 + 351.10 \times T. \text{-----}(13)$$

Finally, the Gibbs energy of formation of  $\text{Na}_3\text{FeO}_3(\text{s})$  was determined as,

$$\Delta_f G^\circ(\text{Na}_3\text{FeO}_3) = -1168629 + 338.34 \times T \quad (298 < T < 720\text{K}) \text{-----}(14)$$

The general error in  $\Delta_f G^\circ(\text{Na}_4\text{FeO}_3)$  was estimated as about  $\pm 2100$  J/mol by Bhat [Ref.14]. So, the final error in  $\Delta_f G^\circ(\text{Na}_3\text{FeO}_3)$  can be estimated as about  $\pm 6$  kJ/mol.

$$\Delta_f G^\circ(\text{Na}_3\text{FeO}_3) \pm 6000 \text{ J/mol} = -1168629 + 338.34 \times T. \text{-----}(15)$$

Of course, the reliability of  $\Delta_f G^\circ(\text{Na}_3\text{FeO}_3)$  is greatly depending on the correctness of  $\Delta_f G^\circ(\text{Na}_4\text{FeO}_3)$ . So, data of  $\Delta_f G^\circ(\text{Na}_3\text{FeO}_3)$  can be modified easily according to the present experimental results if better  $\Delta_f G^\circ(\text{Na}_4\text{FeO}_3)$  becomes available.

## 7. Discussions

Since the MALT2 database and KTH both provided Gibbs energy of formation of  $\text{Na}_3\text{FeO}_3$ , evaluation of all the possible data would be significant. KTH did measurements on Na-Fe-O also by high temperature mass spectrometry. It is found that there exist very large difference between their results and the present results. So, a careful comparison was made between the two experimental in detail as shown in Table 5.



Table 5: Comparison with the KTH experiments

	KTH	JNC
Measurement method	High temperature mass spectrometry	High temperature mass spectrometry
Composition of starting materials before the mass spectrometric test	Na <sub>2</sub> O+FeO+Fe By chemical analysis Na:Fe:O = 45%:20%:35%	Na <sub>4</sub> FeO <sub>3</sub> By X-ray powder diffraction Single phase Na <sub>4</sub> FeO <sub>3</sub>
Sample pre-treatment	Baking at 600-800 K for 30hr.	Baking at 373 K for 20hr.
Sample handling condition	In glove box	In glove box (O <sub>2</sub> , H <sub>2</sub> O < 1-2 ppm)
Testing temperature	876-1101 K 828°C	590-717 K
Knudsen cell	Fe-cell	Pt-cell
Identified main vapor species	Na	Na
Impact energy	No remarks	9.8 eV
Sample composition after the mass spectrometric test	No remarks	Na <sub>4</sub> FeO <sub>3</sub> + Na <sub>3</sub> FeO <sub>3</sub> (9:1) after about 4 hours at 400°C;  Finally, Na <sub>4</sub> FeO <sub>3</sub> completely turn into Na <sub>3</sub> FeO <sub>3</sub> after about 30 hours.
Assumed reaction	Na <sub>4</sub> FeO <sub>3</sub> (s)=Na <sub>3</sub> FeO <sub>3</sub> (s)+Na(g)	Na <sub>4</sub> FeO <sub>3</sub> (s)=Na <sub>3</sub> FeO <sub>3</sub> (s)+Na(g)
Slope in lnP=A+B/T	-29436	-17749
P(Na) at 713 K	About 10 <sup>-5</sup> Pascal. (Calculated from their equation.)	About 1 Pascal.

It should be noted that the most important difference between the two laboratories should be the temperature range in which the sample was treated and measured. As described in the present experiment,  $\text{Na}_4\text{FeO}_3(\text{s})$  was found to decompose to  $\text{Na}_3\text{FeO}_3$  around 573-673 K. It means that it is very hard to keep  $\text{Na}_4\text{FeO}_3(\text{s})$  stable at high temperatures under experimental conditions. Long time operation at higher temperatures over 723 K may greatly change the composition of phase  $\text{Na}_4\text{FeO}_3(\text{s})$ .

As for KTH's experiment, if  $\text{Na}_4\text{FeO}_3(\text{s})$  were really formed from  $\text{Na}_2\text{O}+\text{FeO}+\text{Fe}$  under their conditions, it should have been very unstable at such a high temperatures (876-1101 K). So it is highly possible for the produced  $\text{Na}_4\text{FeO}_3(\text{s})$  rapidly decomposed to other Na-Fe oxides, such as  $\text{Na}_3\text{FeO}_3$ . If this process occurred, the assumption of reaction  $\text{Na}_4\text{FeO}_3(\text{s})=\text{Na}_3\text{FeO}_3(\text{s})+\text{Na}(\text{g})$  would not be valid any more. Further analysis became meaningless also. Unfortunately, it seems that KTH did not noticed this problem. This might be the main cause that resulted in very different sodium vapor pressure as shown in Fig 26.

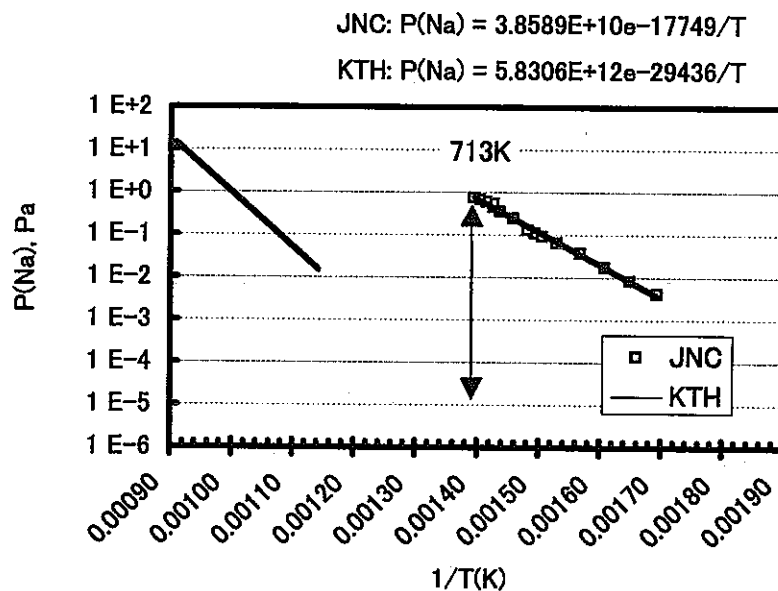


Figure 26: Comparison of sodium vapor pressures over  $\text{Na}_4\text{FeO}_3$  obtained by JNC and KTH, Sweden

Due to these serious concerns about their experiment procedures, it is not proper to accept their experiment results. In the present experiment, special attention was paid to protect the specimen  $\text{Na}_4\text{FeO}_3$ , such as handling in Glove box in which the water vapor and oxygen potential were carefully controlled, and the baking of specimen was carried out at about 373 K, the safe temperature for  $\text{Na}_4\text{FeO}_3$ . These procedures effectively protected  $\text{Na}_4\text{FeO}_3$  and the sodium vapor pressure was successfully measured from 590 to 717 K. So, the analysis of  $\text{Na}_3\text{FeO}_3(\text{s})$  in the present report should be much more reliable.

Another comparison with the MALT2 database was also made because the MALT2 database had been used in JNC to analyze Na-Fe-O system for years. As shown in Fig 27, the Gibbs energy of formation of both  $\text{Na}_4\text{FeO}_3(\text{s})$  and  $\text{Na}_3\text{FeO}_3(\text{s})$  are considerably close to the present results. So, it would be safe to conclude that early studies made by MALT2 would be close to the real situation even though the thermodynamic data of  $\text{Na}_3\text{FeO}_3(\text{s})$  are only estimated values. Of course, thermodynamic data of other Na-Fe oxides such as  $\text{Na}_5\text{FeO}_4$  in the MALT2 database should also be carefully checked later.

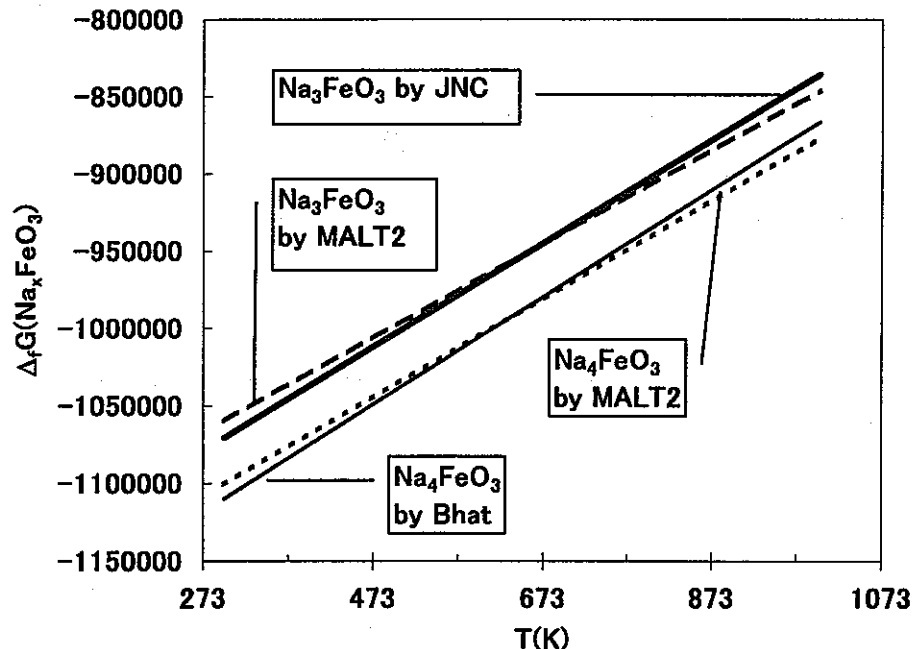


Figure 27: Comparison of Gibbs energies of formation of  $\text{Na}_3\text{FeO}_3$  and  $\text{Na}_4\text{FeO}_3$

## Conclusions

- Theoretical analysis and experimental test have been done on the chemical compatibility of Knudsen cell materials with sodium and its compounds. Platinum was selected to make the Knudsen cell for high temperature mass spectrometer because it shows better anti-corrosion behavior in sodium environment compared to other candidate materials.
- Saturated sodium vapor pressure over pure sodium was measured and high precision results were obtained. The reliability of the whole system was confirmed experimentally. The pressure calibration was carried out based on this experiment results.
- Thermodynamic data of  $\text{Na}_4\text{FeO}_3$  published in reference were summarized.  $\Delta_f G^\circ(\text{Na}_4\text{FeO}_3, \text{s}) \pm 2100 \text{ J/mol} = -1212202 + 351.10 \times T$  given by Bhat was recommended by the authors as probably the best one up to date and is employed to determine  $\Delta_f G^\circ(\text{Na}_3\text{FeO}_3)$ .
- Thermodynamic analysis of reaction  $\text{Na}_4\text{FeO}_3 = \text{Na}_3\text{FeO}_3 + \text{Na}(\text{gas})$  was carried out by high temperature mass spectrometer. Sodium vapor species was found as the main vapor species over  $\text{Na}_4\text{FeO}_3$ . The temperature dependence of partial vapor pressure of sodium was measured from 590 to 717 K.

$$\ln P_{\text{Na}}(\text{Pa}) = 24.376 - 17749 / T (\text{K})$$

According to the present experiment, the Gibbs energy of formation of  $\text{Na}_3\text{FeO}_3$  was evaluated as,

$$\Delta_f G^\circ(\text{Na}_3\text{FeO}_3) = -1168629 + 338.34 \times T \quad (298 < T < 720 \text{K})$$

- It is also found that thermodynamic data of  $\text{Na}_3\text{FeO}_3$  estimated by MALT2 database are considerably close to the present experiment result while those reported by KTH cannot be recommended due to some serious defects in their research works.

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